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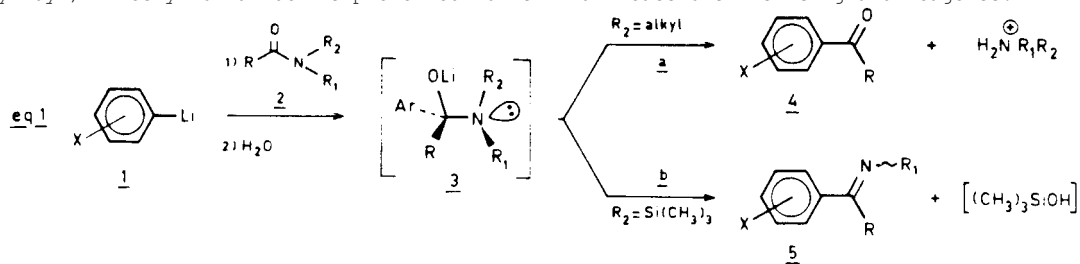
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SYNTHESIS OF ARYLIMINES FROM N-SILYLAMIDES AND ARYL LITHIUM COMPOUNDS

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**Abstract:** Various arylimines were synthesized by the addition of N-silylated-N-alkyl- or N-aryl-amides to aryllithium compounds.

The addition reaction of organolithium compounds 1 to the carbonyl group of N,N-disubstituted amides 2 is well known to yield carbonyl compounds 4 (eq. 1a).<sup>1,2</sup> This reaction is particularly valuable in the synthesis of aldehydes from DMF<sup>1,2</sup> or N-methylformanilide<sup>3</sup> whereas N-(2-pyridyl)-N-methylformamide<sup>4</sup> is preferred for similar reactions with Grignard reagents.

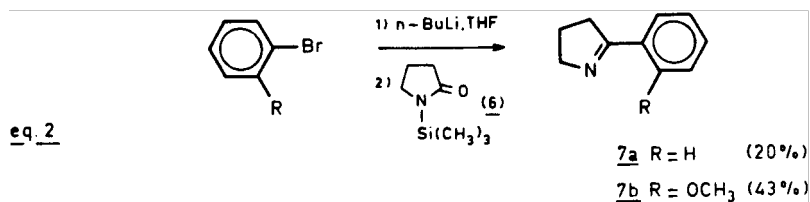


(X = H, CH<sub>3</sub>, OCH<sub>3</sub>; R = H, alkyl, aryl, R<sub>1</sub> = alkyl, aryl)

In connection with synthetic studies using N-silylated-amides<sup>5</sup> 2 (R<sub>2</sub>=Si(CH<sub>3</sub>)<sub>3</sub> and N-silylated-lactams<sup>5</sup> we have found that aryllithium compounds 1 readily react with amides 2 to give imines<sup>6</sup> 5 instead of carbonyl compounds 4 (eq. 1b).

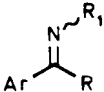
Treatment of a solution of phenyllithium in THF at -78°C with N-methyl-N-trimethylsilyl propionamide, either neat or as a solution in THF, and subsequent warming to room temperature gave after a standard work-up, N-methyl-ethylphenylimine in 73% yield. The results of the conversion of aryllithium compounds with several N-silylated amides are summarized in Table I. The imineformation is strongly dependant on the basicity of the lithium reagent as aryllithium compounds only yielded products derived from deprotonation of the N-silylated acetamides. Isomerically pure imines were obtained from all formamides (entries 6, 10, 11) and N-methyl-N-trimethylsilylacetamides (entries 3, 7). The stereochemical assignment is based on comparison of <sup>1</sup>H-NMR data with those published. For the acetophenone- and 2-acetylfuran-imines (entries 3, 7), the E-configuration was established on basis of the observed coupling constants in the <sup>1</sup>H-NMR spectra (J<sub>H,H</sub> < 1.0 Hz for HC-C=N-CH).<sup>7</sup>

The imines **5** can be reduced in situ to amines [71%, (NaBH<sub>4</sub>, CH<sub>3</sub>OH); 75%, 83% and 60%, (LiAlH<sub>4</sub>, THF) for entries 1, 2, 3 and 4 respectively] or hydrolysed to aldehydes or ketones (e.g. entry 1, 80% phenylethylketone).



The present method also allows preparation of aryl- $\Delta^1$ -pyrrolines **7** from N-silylated-pyrrolidone **6**, although yields are low so far. Thus reaction of phenyllithium with **6** gave 20% of **7** after chromatography (identical with an independently prepared sample<sup>8</sup>) (eq. 2).

**Table I** Synthesis of Arylimines



	Aryl-	R	R <sub>1</sub>	yield(%) <sup>a</sup>	Z/E <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	73	30/70
2	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	60	40/60
3	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	63	0/100
4	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	77	-
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	80	-
6	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	55	0/100
7	C <sub>4</sub> H <sub>3</sub> O	CH <sub>3</sub>	CH <sub>3</sub>	57	0/100
8	C <sub>4</sub> H <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	55	40/60
9	C <sub>4</sub> H <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	79	45/55
10	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	35	0/100
11	(o-OCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	70	0/100

a. Isolated yield by distillation; b. Z/E ratio determined by NMR.

The elucidation of the stereochemical features of this new imine formation and the use of functionalized organolithium reagents is presently under investigation.

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